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Thermoelectric Properties of Semiconducting iridium Silicides

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Semiconducting iridium silicides were synthesized and thermoelectric properties identified. IrSi indicated low resistivity and typical metallic Seebeck was obtained. The Ir_3Si_5 compound showed doping effects with the addition of osmium (p-type) and platinum (n-type), but that represented little influence in the figure of merit. Attempts to dope the compound $IrSi_3$ with platinum were not successful, but the figure of merit was slightly higher in comparison with Ir_3Si_5. A band gap of Eg=1.2± 0.2eV was estimated for the compound Ir_3Si_5. Estimates of power factor values around S.2 µW/cm-K and dimensionless figure of merit ZT values up to 0.1 were determined. Comparison with standard SiGe alloy and thermoelectric properties of each material will be described.

In continuation of our efforts to study and characterize the thermoelectric properties of transition metal silicides for space power applications we decided to prepare good quality samples and investigate doping procedure of iridium silicides. These compounds, duc to the high atomic mass of iridium, were expected to have low thermal conductivity.

Little previous work has been done describing the electrical properties of these materials, probably duc to the fact that the phase diagram was not available and the difficulty to grow these compounds. Only White and Hockings (1971) were able to measure room-temperature resistivity and at 773 K of polycrystalline $IrSi_3$ samples, Recently the phase diagram and the electrical behavior of the silicon-rich side in the iridium-silicon system have been determined (Allevato, 1992,). Growth conditions and semiconducting behavior have also been identified.

For IrSi the resistivity was low and showed almost no dependence with temperature, although semiconducting behavior has been reported in the literature (Shepherd, 1988). Two other silicon rich compounds Ir_4Si_5 and Ir_3Si_4 exhibit resistivities which arc small and increase with temperature, characteristic of metals. The resistivity of two compounds Ir_3Si_5 and $IrSi_3$ suggested semiconducting behavior and were determined to form by peritectic reaction, which required growth from the melt by Bridgman method using compositions slightly silicon-rich, However the thermoelectric properties of the iridium silicides were still undetermined.

IrSi, Ir_3Si_5, and $IrSi_3$ therefore each exhibit some evidence of semiconducting behavior. The present study was performed in order to determine if any of these compounds might be of interest for thermoelectric applications. The possibility to dope such materials and the fact that these mater-ials arc classified as high temperature refractory semi conductor-s were the main thrust of this study.

Experimental Details

Wc used iridium powder (Johnson-Matthey, 99.95%), and silicon lump (99.9995%). Platinum (99.999%) and osmium (99.8%) were used as n-type and p-type dopants respectively. The iridium powder was first arc-melted into beads, in order to avoid weight losses, and then arc-melted together with silicon. Afterwards crystal growth of the samples was carried using Bridgman-like furnace. Both compounds, Ir_3Si_5 and $IrSi_3$, are peritectic and sample preparation was carried out with silicon rich melts of 65 and 75 atomic percent silicon, respectively.

The density of the samples was determined by the Archimedes method where values were repeatable within 0.5%. Densities and X-ray powder patterns were in good agreement with previous results (Allevato, 1992). Resistivity was measured as described elsewhere (McCormack, 1991) by means of the van der Pauw method with temperatures ranging from 300 to 1330 K, neglecting any anisotropy effects. Seebeck coefficient was determined by an apparatus described by Wood et al. (1985). Thermal diffusivity was determined by using a flash lamp illuminating one side of the sample and measuring the time taken for a heat pulse to pass through a small planar disc of material (Wood, 1984). Values of thermal conductivity were then calculated from measured thermal diffusivity, heat capacity and density values.

Results and Discussion

The three compounds IrSi, Ir_3Si_5 and $IrSi_3$ were subject of the present investigation and results obtained are presented in Figures 1-4 and described in the following discussion. Standard SiGe alloy data (Vining, 1991) are included for comparison purposes.

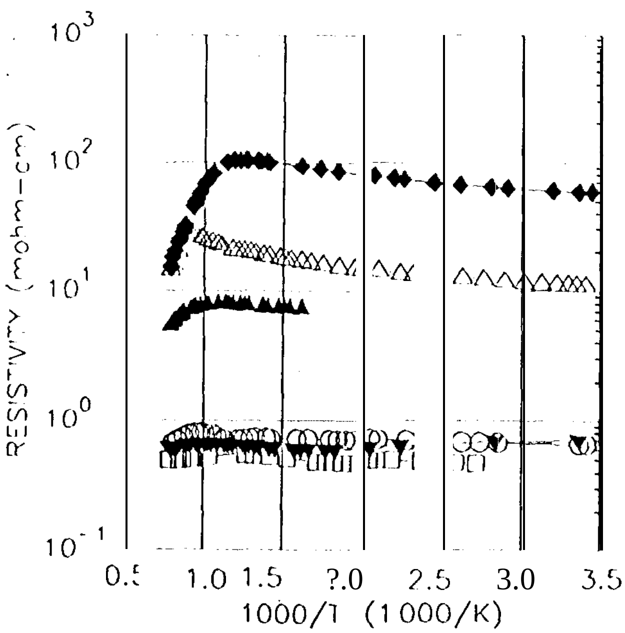

Fig. 1. Electrical resistivity as a function of temperature for IrSi (□); undoped (◆), Os-doped (Δ) and Pt-doped Ir_3Si_5 (Δ); and undoped (▼) and Pt-doped $IrSi_3$ (○).

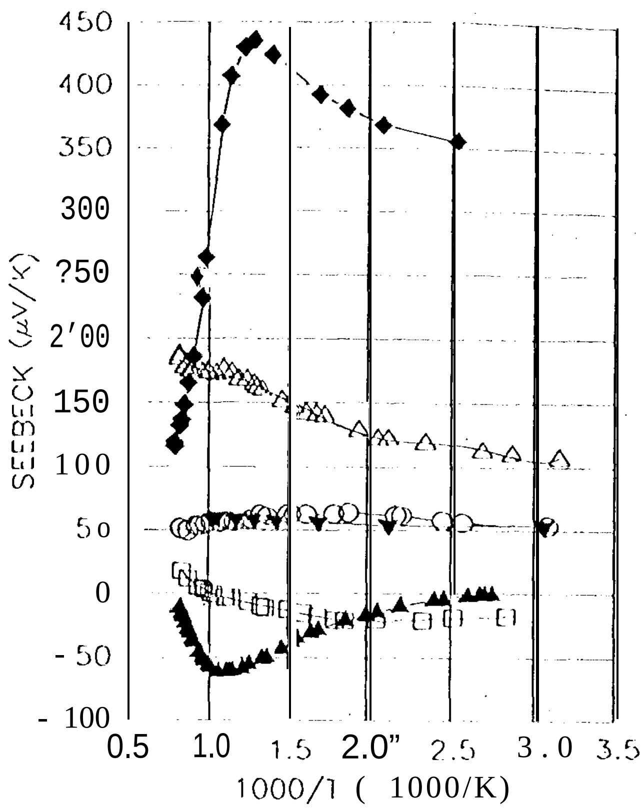

Fig. 2. Seebeck coefficient as a function of temperature for IrSi (□); undoped (◆), Os-doped (Δ) and Pt-doped Ir_3Si_5 (Δ); and undoped (▼) and Pt-doped $IrSi_3$ (○).

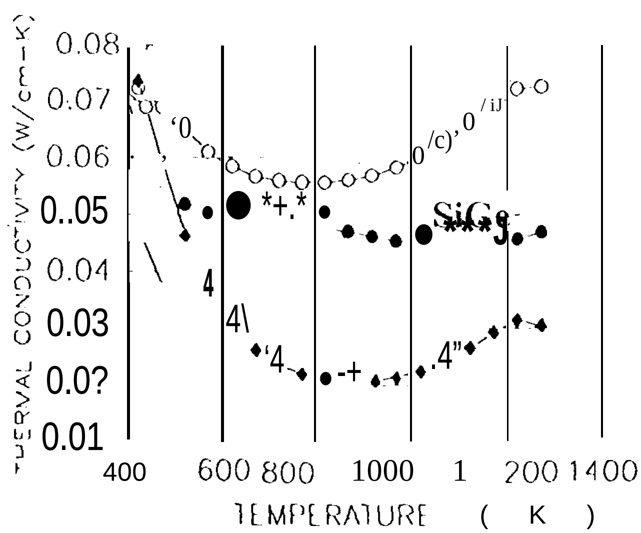

Fig. 3. Thermal conductivity as a function of temperature for Ir_3Si_5 (◆), $IrSi_3$ (○) and SiGe (.).

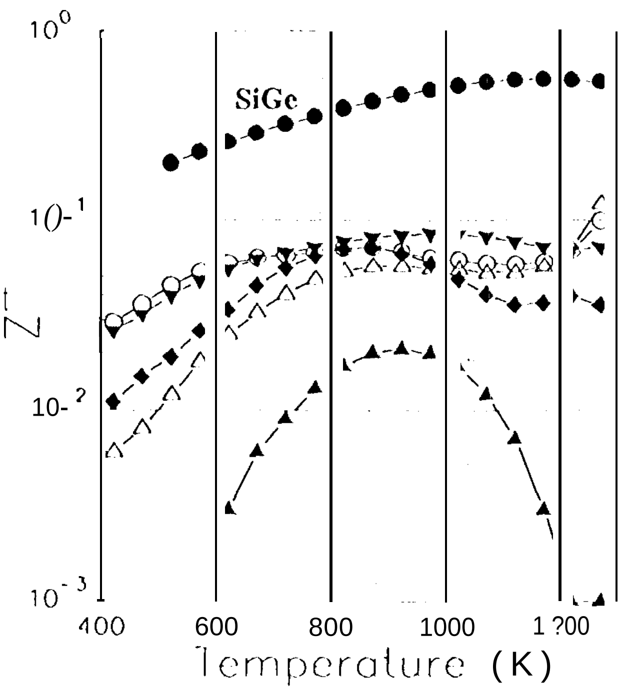

Fig. 4. Dimensionless thermoelectric figure of remit as a function of temperature for undoped (♦), Os-doped (A) and Pt-doped Ir_3Si_5 (A); undoped (V) and P(-doped $IrSi_3$ (O); and SiGe (.),

IrSi

The compound IrSi showed iow resistivity and almost no dependence with temper-atu[c indicating probably the extrinsic region as shown in Fig. 1. liven though a band gap around O. 12eV was reported by Shepherd (1 988), wc saw no evidence of thermal activation in either resistivity and Seebeck results. Measurements of the Seebeck typical of metals, ranging from about -25μV/K to 25p V/K, were obtained. Since resistivity measurements presented no major change with temperature, such small variation in the Seebeck were probably not duc to thermal excitation of carriers.

The electronic contribution for the thermal conductivity of lrSi can be estimated considering the Wiedemann-Franz law and the resistivity value measured, which leads to a minimum value for the thermal conductivity of about 0.009 W/cm-K. The maximum ZT value of 0.042 for lrSi was estimated from

$$ZT_{max} \approx S^2T/\rho\lambda_{el}.$$

Ir_3Si_5

A decrease in the resistivity of the Ir_3Si_5 compound shown in Fig. 1 was observed when doped either with osmium or platinum. The p-type, non-doped Ir_3Si_5 becomes intrinsic around 800K and the sample doped with osmium after 1050K. An estimate of the band gap magnitude, $Eg = 1.2 \pm 0.2$eV, from the slope Eg/2k indicated in Fig. 1 was determined using data from the non-doped sample.

The compound Ir_3Si_5 presents significant drop in the Seebeck coefficient as the material is doped with osmium and platinum. Extrapolation to higher temperatures from of the plot of the non-doped and the platinum doped Ir_3Si_5 sample, anticipate a point where both plots meet and continue together. such typical semiconductor behavior was aiso described by Geballe and Hull (1955) for pure silicon.

The thermal conductivity of the compound Ir_3Si_5 described in Fig. 3 shows measured data with values as iow as 0.02 W/cm-K, haif the thermal conductivity of standard SiGe. At lower temperatures the thermal conductivity drops with increasing temperature indicating a strong lattice contribution. The up turn of the thermal conductivity above 900 K Suggests semiconductor behavior and represents the ambipolar contribution,

Figure 4 shows temperature dependence of the dimensionless figure of merit ZT. Standard SiGe has about five times the ZT value obtained by iridium silicides. Results show that significant doping effects were observed in the Ir_3Si_5 compound and values of Seebeck (100 μV/K to 150μV/K) in the range of typical useful thermoelectric materials were achieved. Nevertheless, doping represented little improvement in the power factor and figure of merit, with maximum values of 1.9 μW/cm-K^2 and 0.072 respectively.

$IrSi_3$

The resistivity of non-doped $IrSi_3$ shows little dependence with temperature and lies close to the values obtained for the metallic IrSi compound. Unlike Ir_3Si_5, doping the compound $IrSi_3$ with platinum resulted in no change on the Seebeck coefficient, suggesting that this element is not an effective dopant. Samples were doped with reasonable amounts of material, about 2%, and further increase of the doping level is expect cd to have little effect on the thermoelectric propel[its.

Both resistivity and Seebeck data appear to be extrinsic but the magnitude of the Seebeck measurements arc relatively higher than obtained for the IrSi and suggests that $IrSi_3$ is not metallic. The carrier concentration is less than typical metals and therefore wc believe it is a semiconductor. Because the intrinsic region was not observed, no estimate of band gap was possible.

$IrSi_3$ has thermal conductivity only slightly higher than standard SiGe, with values above 0.055 W/cm-K, Despite its higher thermal conductivity, the compound $IrSi_3$ shows a slightly higher value of ZT in comparison to Ir_3Si_5, but still not significant compared to SiGe, with power factor as high as 5.2 μW/cm-k^2 ant{ ZT close to *0.1.*

Conclusion

The thermoelectric properties of semiconducting iridium silicides were determined for the first time. IrSi was shown to be metallic and calculated ZT value of 0.042 lies within the range of experimental values obtained for Ir_3Si_5 and $IrSi_3$. Osmium and platinum showed doping effects on the Ir_3Si_5 compound. However platinum doping resulted in no significant change in the resistivity or Seebeck values of the compound $IrSi_3$. Resistivity, Seebeck and thermal conductivity measured plots show features Of classical semiconductor behavior on both Ir_3Si_5 and $IrSi_3$. Band gap for the Ir_3Si_5 was estimated to be around Eg= 1.2±0.2eV.

This study confirmed our hypothesis that iridium silicide compounds would exhibit low thermal conductivity values and semiconducting behavior. Unfortunately for thermoelectric applications, the dimensionless figure of merit ZT value for the iridium silicides hardly exceeds 0.1. The compound $IrSi_3$ has higher thermal conductivity in comparison with its neighboring compound Ir_3Si_5, but still has slightly higher ZT value. It is expected that alloying and doping might decrease the thermal conductivity and improve the figure of merit to some extent, but ZT values exceeding SiGe appear unlikely.

The present study identified iridium silicide compounds that arc high temperature refractory semiconductors and for the first time determined valuable information on the doping process, transport properties and values of ZT. But in the specific, case of thermoelectric materials for space applications they do not represent a major improvement.

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References

White, J. G.; Hockings, E. F. *Inorg. Chem.* ***1971, 10***(9), p. 1934.

Allevato, C.E.; Vining, C. B. In. *Proc. of the 27th Intersociety Energy Conv. Eng. Conf.*, *Society* of Automotive Engineers, Warrendale, PA, 1992; p. 3.493. Also to be published in *J. Alloys and Compounds.*

McCormack, J.; Fleurial, J. P. in *Modern Perspectives on Thermoelectrics and Related Materials*, Allred, D. D.; Vining, C. B.; Slack, G. A., Eds; Mat. Res. Sot. Symp. Proc., Mat. Res. Sot., Pittsburg, PA, 1991, Vol. 234; p. 135.

Wood, C.; Zoltan, D.; Stapfer, G. Rev. *Sci. Instrum.* ***1985***, S6(5), p. 719, Wood, C.; Zoltan, A. *Rev. Sci. Instrum.* 1984, ***55***(2), p. 235.

Vining, C.B.; Laskew, W.; Hanson, J. O.; Van der Beek, R. R.; Gorsuch, P. D. *J. Appl. Phys. 1991, 69(8),* p. *4333,*

Shepherd, F. D.; Spiro, F. D. in *Recent Developments in Infrared Components, SPIE,* 1988, Vol. 915, p. 98.

Geballe, T. H.; Hull, G.W. *Phys. Rev.* ***1955***, 98(4), p. 940.